

REFRACTORY DEGRADATION BY SLAG ATTACK IN COAL GASIFICATION

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Abstract

This research investigates sessile drop interfacial reactions between two refractory materials (high-chromia and alumina) and two synthetic slags (coal and petcoke). Pulverized slag samples were placed at specific microstructure locations on refractory substrates and heated to 1500 °C at $\log(P_{O_2}) = -9$, using a high-speed heating chamber. Cross-sections of the slag/refractory interface indicated unique slag penetration into preferred areas of the refractory and grain dissolution into the slag through a de-bonding mechanism. Initially, the slag attacked both grain boundaries and fine microstructure areas, freeing alumina grains into the slag. Crystalline VO_x formation in the petcoke slag was found to alter the overall liquid composition. Chemical spallation of Cr-containing crystal layer facilitated degradation of the refractory.

Introduction

Coal gasifiers are commercially utilized to produce syngas (CO and H_2) from various carbon feedstock, water, and oxygen. The syngas is then converted to chemicals and electric power. Feedstock materials such as coal, petroleum coke (petcoke), natural gas, or biomass contain numerous minerals and a mixture of ash constituents that may completely or partially liquefy under the gasification conditions ($T = 1300$ to 1600 °C, $P = 2.75$ MPa and $\log(P_{O_2}) = -9$ to -7 [1]). The liquefied ash forms a slag layer that causes degradation of refractory walls. The slag-refractory interactions occur by a combination of chemical dissolution, mechanical erosion, peeling wear, periodical oxidation-reduction reactions, chemistry variation of feedstock, *etc.* [1]. The mineral impurities impart different chemical and physical properties to the slag and can interact differently with the refractory liner. Superior corrosion resistance of high chromia containing refractory over pure alumina has been reported [1, 2, 3]. By cup-type experiments, Rawers *et al.* [2] found the spinel (Al, Cr, Fe) $_3O_4$ phase on the refractory side of the coal slag/high chromia refractory interface in addition to dissolution of Cr into the coal slag.

Thermodynamically stable phases can be predicted from computational aids as shown in Figure 1 (FactSage [4, 5]). At the present experimental temperature (1500 °C), both slags are completely liquid and no solid is expected to form at equilibrium. Crystalline phases, therefore, only form by interfacial reactions with the refractory materials, diffusion, or

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supersaturation. In Figure 1, each homogeneity region is separated by thin dotted lines. For coal slag, there is a small amount of mullite ($2\text{SiO}_2 \cdot 3\text{Al}_2\text{O}_3$) coexisting with molten slag at 1300 °C, however this amount decreases with higher temperatures. The coal slag becomes completely liquid above 1450 °C. Note that the computation for petcoke slag was done without VO_x and KO_x since no interaction data were available in FactSage.

Although a description of the VO_x interaction with slag has not yet been optimized in the current databases of major thermodynamic software packages like FactSage or Thermo-Calc [6], the oxidation state of this transition metal can be predicted from the stability diagram in Figure 2 (FactSage) under the assumption that molten slag does not modify the VO_x stability under the gasification conditions and that the formation kinetics is relatively fast. According to Figure 2, V_2O_3 is likely stable with the molten slag in normal gasification conditions as the melting temperature of V_2O_3 is higher (> 1890 °C [7]). A thermodynamic assessment of the V_2O_3 interaction with slag liquid is underway.

This study focuses on the interfacial reactions between gasifier slags (coal and petcoke) and refractories (90wt.% Cr_2O_3 -10wt.% Al_2O_3 and pure Al_2O_3) on a short-term and long-term basis, by utilizing a hot-stage microscope equipped with an infrared image furnace. The interaction behaviors of the slags on different refractory locations with different surface energies were studied from cross-sectioned samples using Scanning Electron Microscopy (SEM) with X-ray Energy Dispersive Spectroscopy (EDS).

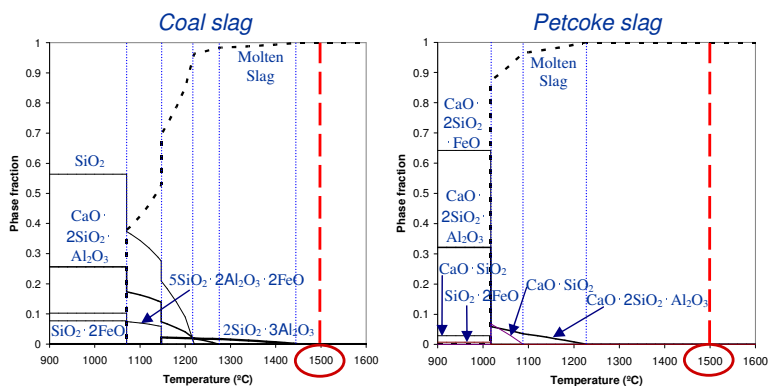


Figure 1: Fractions of stable phases for each specimen over temperature

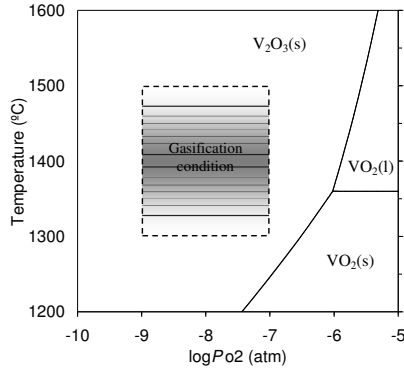


Figure 2: Vanadium oxide stability over oxygen partial pressure indicating V_2O_3 is a stable phase under gasification conditions

Experimental

Two slags studied in this investigation were synthesized. The coal ash slag composition was taken from a report of Selvig and Gibson [8]. The chemistry of the petcoke slag was determined by averaging and normalizing data provided by Bryers [9] and the National Energy Technology Laboratory (NETL) in Albany. The slags were prepared from reagent grade oxide powder mixtures heated above the melting temperature in high purity Ar for two hours. The slags were premelted again under CO/CO_2 ($= 1.8$) atmosphere at 1500 °C for 20 minutes to minimize potential reducing reactions during the experiment. The CO/CO_2 gas mixture provides approximately $\log(P_{O_2}) = -9$ at 1500 °C. The resultant compositions were tested by ICP spectrometry (Table I).

Table I. Chemistry of the Slags Studied

	Petcoke slag (wt.%)	Coal ash slag (wt.%)
SiO_2	25	52
Al_2O_3	7.8	24
CaO	10.1	6.4
Fe_2O_3	10.2	14.5
K_2O	1.2	2.9
V_2O_5	46	-
Total	100.3	99.8

Refractory samples used in this study were sinter-bonded refractories of 90wt.% Cr_2O_3 -10wt.% Al_2O_3 (99.2%) and Al_2O_3 (99.6%). There are generally two structurally distinct regions: grain aggregated parts (up to 3 mm) and matrix regions where fine refractory particles are compacted with bond materials. The porous matrix areas likely lead to chemical dissolution, mechanical erosion and slag penetration due to a large surface area and porosity network throughout the refractory. It should be noted that there are networking pores and microcracks across the grain aggregate as well, though not as extensive as in the matrix areas. SEM micrographs of the refractory surfaces are shown in Figure 3.

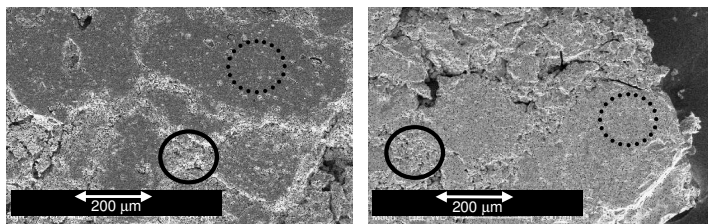


Figure 3: Refractory surfaces of alumina (left) and high-chromia (right) showing two microstructures: fine regions (solid circles) and grain agglomerate (dotted circles)

Slag-refractory interactions were investigated by sessile drop type experiments and elementary analyses over different spatial locations with various grain/particle sizes. A sessile drop (300 to 500 μm) of each slag was placed separately on two different microstructures of a refractory plate (~ 1 mm thick, $1 \mu\text{m}$ surface-finish), and heated at 1500°C for 0 minutes and 10 minutes under the $64\%\text{CO}-36\%\text{CO}_2$ atmosphere. The IR heating chamber of a Confocal Scanning Laser Microscope (CSLM) achieved a heating rate of $77^\circ\text{C}/\text{sec}$ (Figure 4). After each heat treatment, the sample was He-quenched at an average cooling rate of $99^\circ\text{C}/\text{sec}$. The reacted sample surfaces and interfaces were analyzed with SEM-EDS. A temperature gradient, created by a peculiarity of the experimental setup and a spatial deviation from a focal point as the heat source in an ellipsoidal furnace, was estimated by calibration with pure Co ($T_m = 1495^\circ\text{C}$). The average overall deviation of the actual sample temperature against the thermocouple measurement was determined to be $+55^\circ\text{C}$, which is taken into account throughout this study.

The investigation was divided into 16 experiments: 2 slags (coal and petcoke) \times 2 structurally different locations of refractory (grain aggregate and fined particles) \times 2 refractories ($90\text{wt.}\%\text{Cr}_2\text{O}_3-10\text{wt.}\%\text{Al}_2\text{O}_3$ and Al_2O_3) \times 2 holding times (no soaking and 10 minutes). Note that the holding time here corresponds to a length of heat treatment after the designated temperature is reached. Therefore, potential reactions during heating must be also considered.

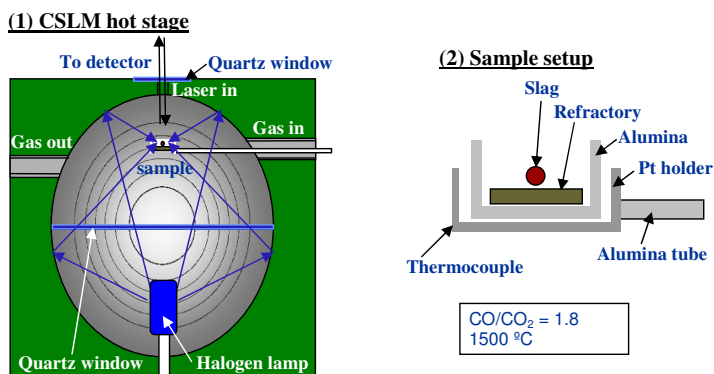


Figure 4: A schematic of CSLM showing (1) a hot stage and (2) sample setup

Results and Discussion

Top-down view SEM images of the slags reacted with distinct microstructures are presented in Figure 5 and Figure 6. Coal slag on a grain agglomerate of both refractories remained on a surface in a semispherical cap after 10 minutes of heat treatments. Penetration into the refractory was observed through the grain regions but the penetration was much smaller than through the fine regions. Al_2O_3 particulates ($10-30 \mu\text{m}$) from the fine matrix of the alumina

refractory were taken up into the coal slag and were washed out on the surface after the remaining slag liquid penetrated into the substrate, whereas the coal slag almost completely penetrated when interacted with the high-chromia refractory. VO_x -based particles formed from the petcoke slag on the refractory surface, altering the remaining liquid chemistry. From EDS results, the V concentration in such a liquid was 15% of that in the original slag (in at.%) from the petcoke sample placed on the high-chromia. No V was detected from the petcoke slag trapped in a pore 500 μm down the high-chromia refractory.

EDS elementary maps for Cr and Si in Figure 7 represent high-chromia refractory substrate and coal slag, respectively. Pore network and fine regions are strongly favored by the slag attack. Penetration through the pores occurred instantly and was more widely expanded underneath the surface compared to the spreading area over the surface.

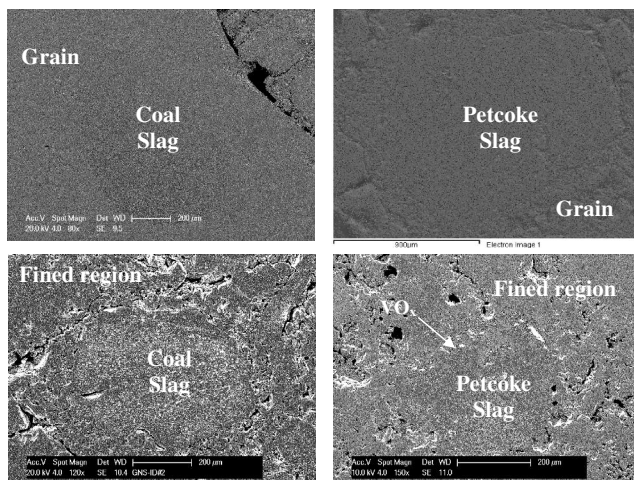


Figure 5: SEM images of slags on high-chromia (10 minutes at 1500 °C)

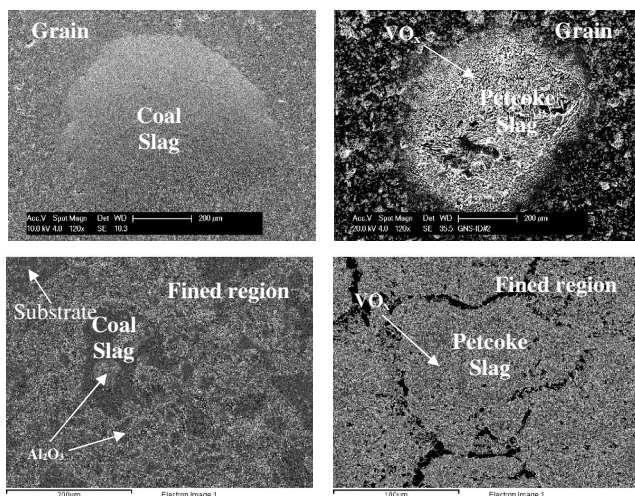


Figure 6: SEM images of slags on alumina (10 minutes at 1500 °C)

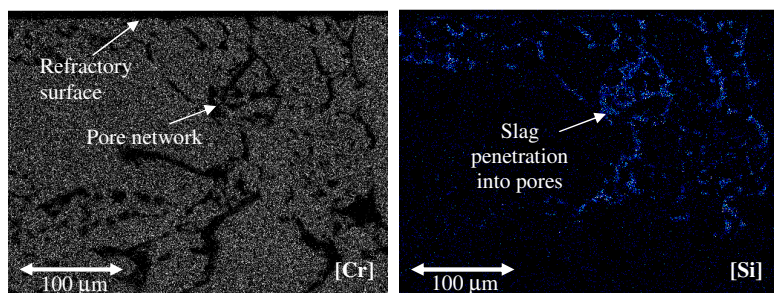


Figure 7: EDS elemental maps revealing pore network (left) and coal slag penetration (right) in high-chromia refractory

Another area vulnerable to refractory degradation was grain boundaries. Figure 8 shows that petcoke slag revealed the grain boundaries of the alumina refractory as it spread over the grain aggregate surface. Although grain agglomerates are relatively more resistant against mechanical erosion and chemical dissolution, alumina grains can still be picked up by severe slag attack targeting the grain boundaries. Fine regions were more susceptible than the grain agglomerates. Slag liquid was promptly sucked into the pores and gaps through the matrix immediately after the slag contacted the refractory. Dissolution of the fine particles enriches the slag liquid and at the same time, larger grains can be carried away into the slag. Figure 9 shows that extensive slag penetration loosened alumina grains on the refractory surface. In practice, continuous slag arrival keeps replenishing the refractory surface and the loosened particles as in Figure 9 can be continuously carried away.

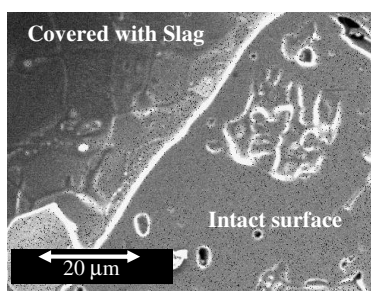


Figure 8: Grain boundaries were revealed as petcoke slag spread over a grain agglomerate of alumina at 1500 °C (after 5min)

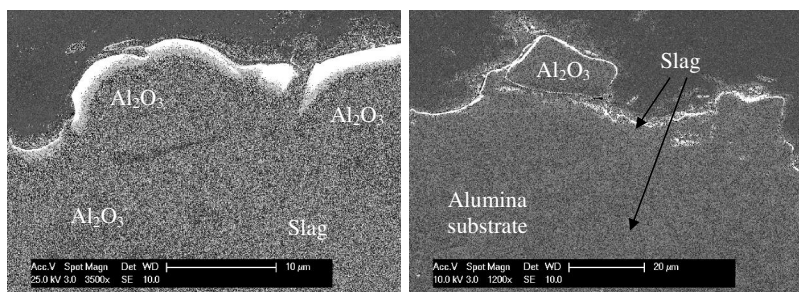


Figure 9: Coal slag penetration into fine regions loosening alumina particulates (0min)

The major constituent of the petcoke slag is vanadium oxide (VO_x). Vanadium is a transition metal with various oxidation states [10, 11, 12]. When the petcoke slag contacts the high-chromia substrate, the fast $\text{VO}_x\text{-Cr}_2\text{O}_3$ interaction causes the immediate formation of the $(\text{Cr, Fe, V})\text{O}_x$ crystalline layer at the slag/refractory interface (Figure 10). The $(\text{Cr, Fe, V})\text{O}_x$ phase grows into the molten slag, which then breaks off and drifts away, although the layer remained continuous during 10 minute-soaking at 1500 °C. As a result, the majority of V stays above/near the surface. V was also found at the bottom of the refractory in most of the cases, which implies early penetration of V-species occurred along with the slag liquid before the formation of VO_x . Fine V-rich spherical particles were also found in the petcoke slag, which probably resulted from supersaturation with Cr_2O_3 and/or Al_2O_3 by refractory dissolution.

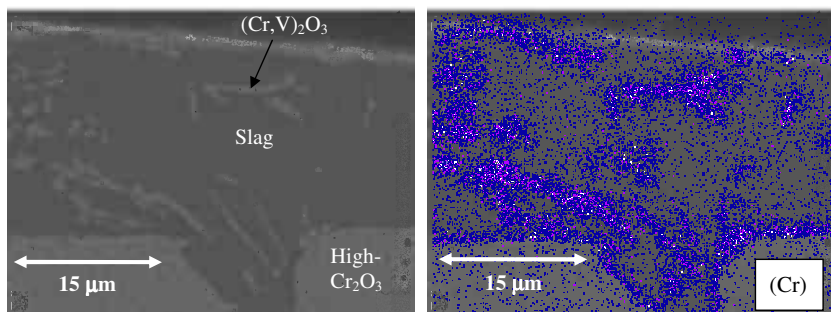


Figure 10: Cross-sectional SEM image (left) and corresponding EDS map (right) showing chemical spallation of $(\text{Cr,V})_2\text{O}_3$ from high-chromia refractory

Conclusion

Weak links of refractory against slag attack are fine regions, pore networks and grain boundaries. Alumina particulates were eroded away by slag surrounding them through grain boundaries, pores and microdefects. Chemical spallation of VO_x -based phase also played a role as product layers at the interface were detached from the high-chromia refractory surface into the slag. The resultant slag liquid after the formation of VO_x was appreciably depleted in V compared to the original slag composition.

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